DIFFUSION OF ARGON AND THE K-AR METHOD

K. PEČ

(Geophysical Institute of Karlovy Universitet, Praha)

and

L. STEGENA

(Geophysical Institute of Loránd Eötvös University)

(Received: 30th August 1966)

SUMMARY

A quantitative discussion of radiogenic argon in platy minerals is given. Argon loss is determined for minerals of various age, diffusivity and thickness.

The diffusivity of a sample can be determined on the basis of the comparison of its K/Ar and Rb/Sr age. For certain minerals, this comparison has yielded diffusivities of the order of 10^{-18} to 10^{-20} $cm^2 s^{-1}$.

As it is well known, the K-Ar radioactive dating method is based on the fact that the radioactive isotope of potassium, K^{40}, decays into Ar^{40} (Fig. 1). The quantity of radiogenic argon is a measure of the age of the rock.

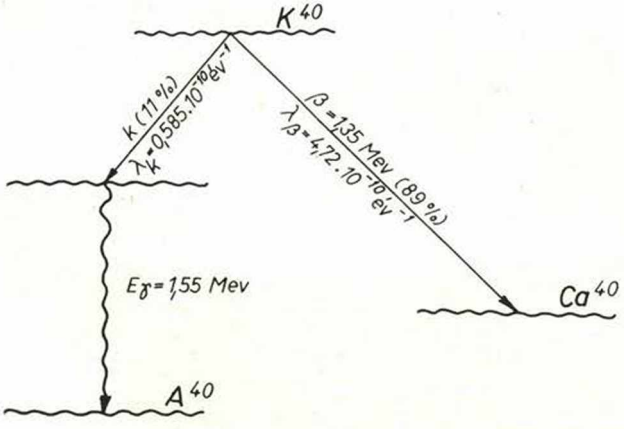

Fig. 1. Decay of K^{40}

Argon, a gas, may leave the rock by diffusion. Experience [(1)–(5)] shows the K-Ar ages of rocks to be often lower than the Rb-Sr ages determined on the same sample. The amount of escaped argon is usually corrected for on the basis of theoretical considerations of argon diffusion.

Fick's Equation of Diffusion is

$$\frac{\partial C}{\partial t} = D \cdot \Delta C, \tag{1}$$

where C is concentration, t is time, D is the coefficient of diffusion, and Δ is the Laplace operator. This equation is formally identical with Fourier's equation of heat transfer. This is why several authors (Fechtig et al. 1960; Reynolds, 1957; Amirkhanov et al. 1960) developed estimates of argon loss by diffusion, based on solutions under appropriate boundary conditions of the heat transfer equation.

The Fick Equation (1) does not, however, hold for the diffusion of radiogenic argon, as it does not take into account the change in Ar concentration owing to the decay of K^{40}, which is superposed upon the change due to diffusion. The amount of Ar^{40} formed per unit volume at an instant t (where t is the time elapsed since the formation of the rock) is

$$\mathrm{Ar} = (\mathrm{K}_0 - \mathrm{K}_t)\,\frac{\lambda_k}{\lambda_k + \lambda_\beta}, \tag{2}$$

where K is the concentration of radioactive potassium, at the instants 0 and t, respectively; λ_k and λ_β are the respective decay constants of Ar^{40} and Ca^{40} formation.

Since

$$\mathrm{K}_t = \mathrm{K}_0\, e^{-(\lambda_k + \lambda_\beta)t}, \tag{3}$$

hence,

$$\mathrm{Ar} = \mathrm{K}_0 \frac{\lambda_k}{\lambda_k + \lambda_\beta}(1 - e^{-(\lambda_k + \lambda_\beta)t}), \tag{4}$$

and

$$\frac{\partial\,\mathrm{Ar}}{\partial t} = \mathrm{K}_0\,\lambda_k\, e^{-(\lambda_k + \lambda_\beta)t} = \mathrm{K}_0'\lambda\, e^{-\lambda t}, \tag{5}$$

where K_0' is that part of the total initial K^{40} content which decays into Ar^{40}:

$$\mathrm{K}_0' = \mathrm{K}_0 \frac{\lambda_k}{\lambda}.$$

This is the amount of change in Ar concentration due to the radiogenic formation of Ar atoms. Hence, the fundamental equation (1) modifies to

$$\frac{\partial\,\mathrm{Ar}}{\partial t} = D\Delta\mathrm{Ar} + \mathrm{K}_0'\lambda\, e^{-\lambda t}. \tag{6}$$

This is the equation to be solved under the proper initial and boundary conditions in order to assess quantitatively the loss of Ar^{40} by diffusion.

An approximate solution has been given by Wrage (1962) who started from an ingenious theorem by Kármán. This theorem presupposes that Ar concentration is not changed by diffusion except in a thin layer adjacent to the surface of the grain under consideration. This assumption, however, often fails to be satisfied, as shall be proved below; this circumstance is shown also in Fig. 3, where the concentration drop brought about by diffusion is seen to penetrate also into the interior of the mineral grain.

Nicolayson (1957) and Wasserburg (1957) have given rigorous solutions for spherical mineral grains. However, most minerals entering into consideration (the micas in the first place) assume platy rather than spheroidal forms.

It is therefore of interest to seek a solution for platy mineral grains.

Assume the thickness of the mineral grain to be much smaller than its other two dimensions. The diffusion current can then be considered unidimensional:

$$\frac{\partial \mathrm{Ar}}{\partial t} = D \frac{\partial^2 \mathrm{Ar}}{\partial x^2} + \mathrm{K}_0' \lambda e^{-\lambda t}. \tag{7}$$

Let

$$\mathrm{Ar}(x, o) = 0, \tag{8}$$

be the initial condition; let further

$$\mathrm{Ar}(+h, t) = 0 \tag{9}$$

and

$$\mathrm{Ar}(-h, t) = 0, \tag{10}$$

be the boundary conditions (Fig. 2). The initial condition is trivial. The boundary conditions express the assumption that the concentration due to diffusion is zero at the grain surface. In other words, the grain is supposed to be surrounded by a medium of infinite diffusivity with respect to argon. In reality, the potassium-bearing mineral grain is embedded in a rock matrix. Notwithstanding, it has been found that resistance to diffusion takes a sudden drop at the grain boundary: consequently, argon is able to escape from the grain. This has been proved e.g. by Gentner's and Kley's experiments (1957) who found a gradual loss of argon on grinding a sample to increasingly fine grain sizes. $\mathrm{Ar}(+h, t) = 0$ gives, as a matter of fact, the maximum possible

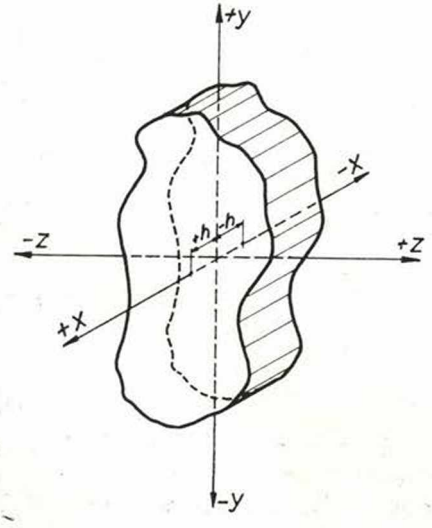

Fig. 2.

argon loss: the actual argon loss is a more or less close approximation of that value.

Under the above boundary conditions, the solution (see Appendix) takes the form

$$\mathrm{Ar}\,(x,t) = -\mathrm{K}_0\left(1-\frac{\cos\sqrt{\frac{\lambda h^2}{D}}\,\frac{x}{h}}{\cos\sqrt{\frac{\lambda h^2}{D}}}\right)e^{-\lambda t}+$$

$$+\frac{2\,\mathrm{K}_0'}{\pi}\sum_{m=1}^{\infty}(1-)^{m+1}\frac{\cos\left[(m-1/2)\pi\,\frac{x}{h}\right]}{1-(m-1/2)^2\,\frac{D\pi^2}{h^2\lambda}}\cdot\frac{e^{-(m-1/2)^2\,\pi^2\frac{Dt}{h^2}}}{m-1/2}. \tag{11}$$

(11) yields the concentration of argon as a function of the variables t and x/h, provided the parameter h^2/D is known. — Fig. 3. shows concentrations $\mathrm{Ar}(x,\,t)$ obtained by means of a computer, for various values of h_2/D and $t\cdot\lambda$ has been taken as $1{,}7\cdot10^{-17}\,s^{-1}$ [Wetherill et al., (1957)]. The average Ar^{40} concentration over the interval from $-\,h$ to $+\,h$ can be obtained as the integral mean

$$[\mathrm{Ar}]_{+h}^{-h} = \frac{1}{2h}\int_{+h}^{-h}\mathrm{Ar}\,(x,t)\,dx. \tag{12}$$

The Ar^{40} concentration that would prevail if there were no diffusion can be computed on the basis of (6) with $D = 0$ from

$$\frac{\partial\,\mathrm{Ar}_{D=0}}{\partial t} = \mathrm{K}_0'\lambda\,e^{-\lambda t}; \tag{13}$$

we have

$$\mathrm{Ar}_{\,D=0} = -\mathrm{K}_0\,e^{-\lambda t}+\mathrm{const}, \tag{14}$$

where the constant is, by the assumption that

$$\mathrm{Ar}\,(x,o) = 0 \tag{15}$$

equal to K_0'. Hence, (14) may be rewritten as

$$\mathrm{Ar}_{\,D=0} = \mathrm{K}_0'(1-e^{-\lambda t}). \tag{16}$$

(16) subtracted from (12) yields argon loss attributable to diffusion: the latter, divided by (16), is specific argon loss.

In Table 1., percentual argon loss is stated for various ages and h^2/D parameters.

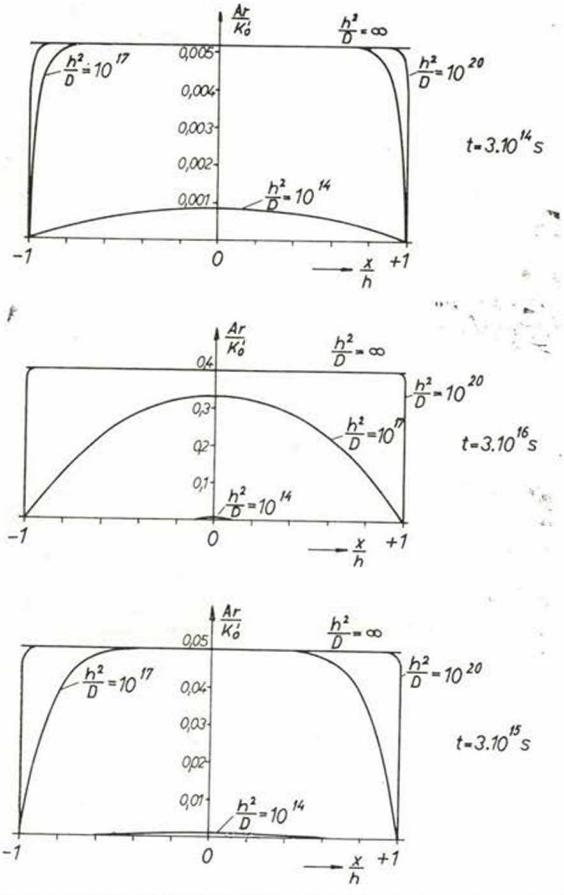

Fig. 3. Variation of argon concentration in platy minerals, in function of thickness, diffusivity and age.

Table 1. Argon loss due to diffusion, in percent, for platy mineral grains of thickness 2h and diffusivity D, for life spans of 10, 100, 1000 and 10 000 million years.

h^2/D (s)	t(s)→3 · 10¹⁴	3 · 10¹⁵	3 · 10¹⁶	3 · 10¹⁷
10^{20}	0	0	2	6
10^{17}	4	13	43	99
10^{14}	88	99	100	100
10^{11}	100	100	100	100

The table reveals that

for $h^2/D \geqq 10^{20}$ s there occurs no argon loss within the time intervals that enter into consideration ($3 \cdot 10^{14}$ to $3 \cdot 10^{16}$ years);

for $h^2/D \leqq 10^{14}$ s, the K/Ar dating method yields illusory results owing to excessive argon loss.

h ranges in practice from 10^{-2} to 10^{0} cm. For the mineral species that enter into consideration, D can be derived on the basis of the above computation for samples which have been dated with both the K/Ar and the Rb/Sr method.

Table. 2 lists the results of such determinations by Gast, Kulp and Long (1958). Assuming the Rb/Sr ages as free of error, one can determine by (16) the specific Ar^{40} loss from the K/Ar ages. Confronting the loss values thus obtained with (16) or (12) or Table 1, one finds that for the age of the samples (7 to $8 \cdot 10^{16}$ s) the measured argon loss of 3.2 to 7.2 percent is to be expected at $h^2/D \sim 10^{20}$ s. As in the samples in question, h^2 amounted to between 10^{0} and 10^{-2} cm, we find $D \sim 10^{-18}$ to 10^{-20} $cm^2 \cdot s^{-1}$. The calculation could have been carried out to a higher degree of accuracy, but this would have been illusory in view of the accuracy range of the measurements.

Table 2. K/Ar and Rb/Sr ages of Wyoming and Montana rocks, after Gast, Kulp and Long, and the calculated values of argon loss.

Mark of sample	K/Ar age	Rb/Sr age	Ar^{40} loss %
	10^6 years		
Gm YB 11	2470 ± 50	2800 ± 50	5.7
Gm YB 5	2290 ± 60	2530 ± 45	5.0
Gm YB 16	2520 ± 50	2700 ± 67	3.2
Gsm YB 17	2340 ± 50	2750 ± 60	7.2
Gsm YB 20	2540 ± 50	2760 ± 60	3.6
Gm X 10	2440 ± 60	2680 ± 90	4.2
Gm X 11	2340 ± 50	2650 ± 45	5.7
Gsm X 12	2160 ± 50	2350 ± 66	4.7

Similar results have been obtained by Fechtig, Gentner and Zähringer (1960) (Table 3). The results are rather encouraging for the K/Ar method as the h^2/D parameter is seen not to fall below the desirable 10^{20} s except for grains with a $h < 1$ mm.

Table 3. Diffusion coefficients of some minerals at room temperature. After Fechtig, Gentner and Zähringer

	D ($cm^2 s^{-1}$)
Fluorspar	$5 \cdot 10^{-23}$
Anorthite	$1{,}5 \cdot 10^{-22}$
Augite	$1 \cdot 10^{-22}$
Margarite	$3 \cdot 10^{-25}$

Other authors (Hurley et al., 1962) have measured h^2/D values in the range of 0.1 to 2.10^{16} s. In such rocks, argon loss may be fairly high.

Metamorphic processes cause a rise in temperature and pressure and also in the D parameter. The pressure-dependence of D may be neglected beside its temperature-dependence (Stegena, 1966). D increases with temperature as

$$D = D_0 e^{-Q/RT}. \tag{17}$$

The energy of activation, Q, varies from rock to rock. It is fairly high: 50 to $100 \cdot 10^3$ cal/gram-atom (Amirkhanov et al. 1960, Gerling, Morozova 1957, Evernden et al. 1960.). This explains how Goles, Fish and Anders (1960) could find 10^6 to 10^8 s for h^2/D at 600 to 1500 degrees Kelvin.

Starting from formulae (16), (12) and (17), the argon loss of a rock whose diffusivity, D, changes abruptly in time can also be computed. This permits metamorphic processes to be modeled. It is the authors' intention to return to this problem in a paper to follow.

Appendix (K. Peč)

Let us solve the equation

$$\frac{\partial \mathrm{Ar}}{\partial t} = D \frac{\partial^2 \mathrm{Ar}}{\partial x^2} + \mathrm{K}_0' \lambda e^{-\lambda t}, \tag{6}$$

under the following initial and boundary conditions:

$$\mathrm{Ar}(x, 0) = 0, \tag{8}$$

$$\mathrm{Ar}(+h, t) = 0, \tag{9}$$

$$\mathrm{Ar}(-h, t) = 0. \tag{10}$$

We may write up the following Laplace transforms:

$$\mathfrak{L}\,[\mathrm{Ar}(x, t)] = \mathrm{Ar}^*(x,p) = \int_0^\infty \mathrm{Ar}(x, t)\, e^{-pt}\, dt$$

$$\mathfrak{L}\,[e^{-\lambda t}] = \frac{1}{p+\lambda}$$

$$\mathfrak{L}\left[\frac{\partial \mathrm{Ar}}{\partial t}\right] = p\,\mathrm{Ar}^*(x, p) - \mathrm{Ar}(x,o).$$

Substituting into (6) we get

$$p\,\mathrm{Ar}^*(x, p) - \mathrm{Ar}(x, o) = D \frac{d^2 \mathrm{Ar}^*}{dx^2} + \frac{\mathrm{K}_0' \lambda}{p+\lambda},$$

$$\frac{d^2 \mathrm{Ar}}{dx^2} = \frac{1}{D}\left[p\,\mathrm{Ar}^* - \frac{\mathrm{K}_0' \lambda}{p+\lambda}\right] = \frac{p}{D}\,\mathrm{Ar}^* - \frac{\mathrm{K}_0' \lambda}{p(p+\lambda)}.$$

Introducing the notation

$$B(x, p) = \mathrm{Ar}^*(x, p) - \frac{\mathrm{K}_0' \lambda}{p(p+\lambda)}$$

we may rewrite (6) as

$$\frac{d^2B}{dx^2} = \frac{p}{D} B.$$

This equation solves to

$$B(x, p) = A_1 e^{-\sqrt{\frac{p}{D}}x} + A_2 e^{+\sqrt{\frac{p}{D}}x}.$$

The Laplace transforms of (8), (9) and (10) are

$$\mathrm{Ar}^*(+h, p) = \mathrm{Ar}^*(-h, p) = 0,$$

$$\mathrm{Ar}^*(x, p) = \frac{\mathrm{K}_0' \lambda}{p(p+\lambda)} + A_1 e^{-\sqrt{\frac{p}{D}}x} + A_2 e^{+\sqrt{\frac{p}{D}}x}.$$

These equations imply the following:

$$\frac{\mathrm{K}_0' \lambda}{p(p+\lambda)} + A_1 e^{-\sqrt{\frac{p}{D}}h} + A_2 e^{+\sqrt{\frac{p}{D}}h} = 0,$$

$$\frac{\mathrm{K}_0' \lambda}{p(p+\lambda)} + A_1 e^{+\sqrt{\frac{p}{D}}h} + A_2 e^{-\sqrt{\frac{p}{D}}h} = 0.$$

Their solution is

$$A_1 = A_2 = -\frac{\mathrm{K}_0' \lambda}{2p(p+\lambda)} \frac{1}{ch\sqrt{\frac{p}{D}}h}.$$

Hence,

$$\mathrm{Ar}^*(x, p) = \frac{\mathrm{K}_0' \lambda}{p(p+\lambda)} \left[1 - \frac{ch\sqrt{\frac{p}{D}}x}{ch\sqrt{\frac{p}{D}}h} \right].$$

Retransforming yields

$$\mathrm{Ar}(x, t) = \frac{\mathrm{K}_0' \lambda}{2\pi i} \int_{p-i\infty}^{p+i\infty} \frac{1}{p(p+\lambda)} \left[1 - \frac{ch\sqrt{\frac{p}{D}}x}{ch\sqrt{\frac{p}{D}}h} \right] e^{pt} dp,$$

and the zeroes of the integrand are at

$$p = 0, -\lambda; \sqrt{\frac{p}{D}}h = \pm i(2m-1)\frac{\pi}{2} \quad (m = 1, 2, 3 \ldots)$$

Evaluation of the integral by means of the Residue Theorem yields

$$\mathrm{Ar}(x,t) = -\mathrm{K}_0'\left(1 - \frac{\cos\sqrt{\frac{\lambda h^2}{D}}\frac{x}{h}}{\cos\sqrt{\frac{\lambda h^2}{D}}}\right)e^{-\lambda t} +$$

$$+\frac{2\mathrm{K}_0'}{\pi}\sum_{m+1}^{\infty}(-1)^{m+1}\frac{\cos\left[(m-1/2)\pi\frac{x}{h}\right]}{1-(m-1/2)^2\frac{D\pi^2}{h^2\lambda}}\frac{e^{-\left(m-\frac{1}{2}\right)^2\pi^2\frac{Dt}{h^2}}}{m-\frac{1}{2}}.$$

This is the answer to the problem raised at the beginning.

REFERENCES

Kulp, J. L. – Engels, N. 1963: Discordances in K-Ar and Rb-Sr isotopic ages. – *in* Radioactive dating, Vienna, I. A. E. Agency.

Mehnert, K. R. 1958: Argonbestimmungen an Kaliummineralien. VI. G. C. A. 14. p. 105 – 113

Lippolt, H. J. – Gentner, W. 1962: Argonbestimmungen an Kaliummineralien. X. – G. C. A. 26. p. 1247 – 53.

Gast, P. W. – Kulp, J. L. – Long, L. 1958: Absolute age of early Precambrian rocks in the Bighorn Basin of Wyoming and Montana, and Southern Manitoba. – T. A. G. U. 39. 2.

Fechtig, H. – Gentner, W. – Zähringer, J. 1960: Diffusionsverluste von Argon in Mineralien und ihre Auswirkung auf die Kalium-Argon Altersbestimmungen. – G. C. A. 19. p. 70 – 79.

Reynolds, J. H. 1957.: Comparative study of argon content and argon diffusion in mica and feldspar. – G. C. A. 12. p. 177 – 184.

Amirkhanov, Kh. I. – Brandt, S. B. – Bartnitskiy, Ye. N. 1960.: Radiogennyy argon v mineralakh i gornykh porodakh. – Makhachkala. Akad. Nauk. SSSR Dagestan. Filial, p. 202.

Wrage, E. G. 1962.: Ein Näherungsverfahren zur Lösung von Diffusionsproblemen. – G. C. A. 26. p. 61 – 66.

Nicolayson, L. O. 1957.: Solid diffusion in radioactive minerals and the measurement of absolute age. G. C. A. 11. 41.

Wasserburg, G. J. 1957.: Argon 40 – potassium 40 dating. *in* Nuclear Geology.

Gentner, W. – Kley, W. 1957.: Argonbestimmungen an Kaliummineralien IV. – G. C. A. 12. p. 323.

Wetherhill, G. W. et al. 1956.: Decay constans of K^{40} as determined by the radiogenic argon content of potassium minerals. Phys. Rev. 103. 4. p. 987–989.

Hurley, P. M. – Heezen, B. C. – Pinson, W. H. – Fairbairn, H. W. 1962.: K-Ar values in pelagic sediments of the North Atlantic. – G. C. A. jun. 26. 67.

Stegena, L. 1966.: On the possibility of diffusion at the M-discontinuity. – Boll. di Geofisica, 32. p. 309–317.

Goles, G. G. – Fish, R. A. – Anders, E. 1960.: The former environment of stone meteorites as deduced from $K^{40}-Ar^{40}$ ages. – G. C. A. 19. p. 177–195.

Gerling, E. K. – Morozova, I. M. 1957.: Opredeleniye energii aktivatsii vydeleniya argona iz slyud. – Geokhimia, 4. p. 304–311.

Evernden, J. F. – Curtis, H. – Kistler, R. W. – Obradovich, J. 1960.: Argon diffusion in glauconite, microcline, sanidine, leucite and phlogopite. – Am. J. Sci. 258. 583.